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METALLIC REACTOR TUBE WITH CATALYTIC COATING

[Metallisches Reaktionsrohr mit Katalytischer Beschichtung]

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The invention relates to a metallic reactor tube with catalytic coating preferably on the tube inner wall, tube-bundle reactors with coated reactor tubes, a coating method, as well as a use of the reactor tube or the tube-bundle reactor in the catalytic gas-phase oxidation for the production of (meth)acrolein and/or (meth)acrylic acid.

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A plurality of chemical reactions is performed in heterogeneous catalysis in reactor tubes. The catalysts are usually used as uniform or carrier catalysts and are introduced as bulk material into the reactor tubes. Filled reactor tubes, however, are disadvantageous, especially with respect to the increased pressure drop, as well as the increased weight. As a rule, this makes a larger wall thickness necessary, with negative effects on the heat transfer. These disadvantages are overcome by the application of a catalytic coating on the tube inner walls.

In WO 97/25146 a catalytically active coating is disclosed that is made from a layer composite with a metallic base body, for example, the inside of a reactor tube, adhesive, and catalytically active cover layer made from, in particular, oxide-ceramic catalyst material. In order to prevent peeling of the catalytically active cover layer with varying temperature conditions, it is then absolutely necessary to first apply an adhesive with an essentially metallic composition onto the metallic base body.

From DE-OS 21 18 871 it is known to reduce the formation of secondary products for the production of carboxylic acids or their anhydrides through gas-phase-catalytic oxidation of aromatic or unsaturated, aliphatic hydrocarbons in the presence of carrier catalysts containing vanadine pentoxide in a tube-bundle reactor in that the inner wall of the tubes is coated at least partially with a catalytic mass that contains titanium dioxide, advantageously in the mixture with vanadine pentoxide. The processing products are obtained with great purity and high yields. The description contains no suggestions for a reduction of the hot-point temperatures in the tubes.

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* [Numbers in right margin indicate pagination of the original text.]

A heterogeneous, catalyzed reaction that is important industrially is the catalytic gas-phase oxidation of C₁-C₆ alkanes, C₂-C₆ alkenes, C₁-C₆ alkanols, and/or alkanals and/or precursors of these materials for the production of (meth)acrolein and/or (meth)acrylic acid. These reactions progress strongly exothermally, which is why it is necessary for a selective conversion, due to a plurality of possible parallel or consecutive reactions, to control the progression of the reaction temperature. For temperature regulation, the reactor tubes are surrounded by a heat-carrier medium, for example, by a molten salt. Despite this temperature regulation, due to the bulk catalyst material, so-called hot spots are formed with elevated temperature in comparison with the rest of the bulk catalyst material. This, on one hand, reduces the service life of the catalyst in this contact tube section and, on the other hand, negatively affects the selectivity of the acrolein acrylic acid formation.

Various countermeasures for overcoming the mentioned disadvantage have already been recommended in the prior art and are described, for example, in DE-A-44 31 949. One proposal consists in reducing the diameter of the contact tubes in order to increase the heat dissipation per unit of volume of the catalyst. A disadvantage in this method, however, is that it necessarily increases the number of contact tubes filled with catalyst required for a given production capacity, which increases both the production costs of the reactor and also the time period required for filling and emptying the contact tubes in the catalyst.

According to another proposed method, an attempt is made to suppress the formation of the hot spots /3 in that the volume-specific activity of the catalytic charge is varied along the contact tubes. This procedure, however, requires the use of either at least two catalysts of different activity or the co-use of inert material. In addition, this procedure complicates the filling of the contact tubes. Another obvious possibility for reducing the hot-spot formation consists in reducing the acrolein load on the reactor. This measure, however, simultaneously reduces the space-time yield of the desired product.

In DE-A-44 31 949, a reduction of the hot-spot temperatures in the tubes of a tube reactor with a heat-exchanging-agent circuit in the space surrounding the contact tubes through a meander-shaped guidance of the heat-exchanging agent in concurrent flow with the reaction gases, as well as by maintaining certain low temperature differences of the heat-exchanging agent from the inlet point up to the outlet point from the reactor.

The task of the invention is to provide a reactor tube or a tube-bundle reactor with reactor tubes that are constructed such that, for the execution of heterogeneous catalyzed gas-phase oxidation in such reactor tubes, the occurrence of "hot spots" is predominantly or completely prevented. This task shall be achieved easily through a suitable formation of the reactor tubes without special requirements on the temperature profile and flow guidance of the heat-exchanging-means circuit.

The task is achieved according to the invention by the provision of a metallic reactor tube with catalytic coating, wherein the coating contains a multi-metal oxide mass that is deposited directly on the reactor tube.

It was found surprisingly that a coating that contains a multi-metal oxide mass and that is deposited /4
directly onto a metallic reactor tube without an adhesive intermediate layer presents a composite with long-term stability that is stable at temperatures up to approximately 600°C, like those that typically occur under catalytic gas-phase oxidation.

Also, a coating process shall be provided for the production of corresponding metallic reactor tubes or tube-bundle reactors.

The term "multi-metal oxide mass" used presently designates oxidic mixtures that contain two or more, preferably three or more chemical elements, wherein, in general, no more than 50 different chemical elements are contained in a percentage of more than 1 wt%. The transition-metal elements molybdenum and bismuth are always contained in the multi-metal oxide masses used according to the

invention. Typically, the multi-metal oxide masses are not simple physical mixtures of oxides of the elementary constituents, but are instead heterogeneous mixtures of complex poly-compounds of these elements.

The multi-metal oxide masses used according to the invention usually contain molybdenum, calculated as MoO_3 , in a percentage of 20-90 wt%, preferably 30-80 wt%, especially preferably 40-70 wt%.

The catalytic coating containing the multi-metal oxide mass is deposited directly on the reactor tube, i.e., without an auxiliary carrier or adhesive intermediate layers being arranged therebetween.

Preferably, the tube inner wall of the metallic reactor tube is provided with the catalytic coating.

With respect to the metallic materials for the reactor tube, there are, in principle, no restrictions, but /5
steel, in particular, stainless steel, such as V₂A steel, as well as ferritic steel, is preferred.

The catalytic coating according to the invention advantageously has a layer thickness of 10-1000 μm , preferably 20-500 μm , especially preferably 50-350 μm .

In one preferred constitution, the invention relates to tube-bundle reactors with metallic reactor tubes that are provided according to the above constructions with a catalytic coating that contains a multi-metal oxide mass deposited directly on the reactor tubes, preferably on the tube inner wall.

Although the reactor tubes of the tube-bundle reactor can have any cross section, as a rule, they are round, in particular, circular. The tube inner diameter equals advantageously 0.2-70 mm, in particular, 10-50 mm, especially preferably 15-30 mm. The tube-bundle reactor can contain, as a rule, up to 50,000 reactor tubes, preferably 50-40,000, especially preferably 500-30,000 reactor tubes. The tube length equals, as a rule, 0.1-10 m, preferably 0.3-8 m, especially preferably 0.5-6 m.

According to one special embodiment, it is possible to introduce a bulk material from multi-metal oxide uniform catalysts or coated catalysts into the reactor tubes, preferably in their entirety, in

particular, with a filling height of 5-90%, advantageously of 10-70%, especially of 20-50% of the entire reactor tube length. The bulk catalyst material is advantageously deposited in the region on the gas-outlet side.

According to another preferred embodiment, a second reactor, in particular, a tube-bundle reactor that is provided with bulk material from multi-metal oxide uniform catalysts or coated catalysts is connected downstream to a tube-bundle reactor with completely or partially coated reactor tubes. This /6 arrangement of two reactors connected one behind the other offers the advantage that the reaction can be processed for different, especially adapted processing conditions according to the degree of progress. In particular, in the first reactor whose tubes carry the catalytic coating according to the invention, due to the prevention of the risk of hot spots, temperatures that are higher as a rule by approximately 20-100°C in comparison with conventional gas-phase oxidation for forming (meth)acrolein and/or (meth)acrylic acid, of typically 200-450°C, can be processed. Therefore, due to improved desorption, less educt losses due to total combustion take place.

The coating method according to the invention comprises the following steps:

- (1) Production of solutions, emulsions, and/or dispersions of elements and/or element compounds of the elements present in multi-metal oxide catalysts and/or catalyst precursors,
- (2) Optional deposition of adhesives, bonding agents, viscosity regulators, and/or pH-regulating means in the solutions, emulsions, and/or dispersions,
- (3) Deposition of solutions, emulsions, and/or dispersions onto the reactor tube or the reactor tubes of the tube-bundle reactor, preferably on their inside, advantageously by spraying or dipping, and
- (4) Heating of the coated reactor tube, optionally in the presence of inert or reactive gases, to a temperature in the range of 20-1500°C, preferably to 200-400°C, for drying and optionally sintering or calcining the multi-metal oxide catalysts and/or catalyst precursors.

Initially, the production of a fluid output mixture is performed in the form of a solution, emulsion, and/or dispersion according to the way described in DE-A 198 05 719. The fluid mixtures contain, in general, a fluid chemical component that is used as a solvent, emulsifying auxiliary agent, or dispersing auxiliary agent for the additional components of the mixture. For this purpose, advantageously water is used and/or one or more organic compounds whose boiling point or sublimation temperature under normal pressure is $>100^{\circ}\text{C}$, advantageously $>150^{\circ}\text{C}$. Advantageously, the organic percentage of the fluid, chemical components to be used according to the invention equals 10-80 wt%, in particular, 10-70 wt%, and especially preferably 20-50 wt%. /7

Apart from the chemical elements of the solvent or dispersing auxiliary agent, the fluid mixtures contain one or more, preferably 2 or more, preferably 3 or more chemical elements, wherein, in general, but not more than 50 different chemical elements are contained each with a quantity of more than 1 wt%. Preferably, the chemical elements in the mixtures are provided in a very intimate mixture, e.g., in the form of a mixture made from various miscible solutions, intimate emulsions with small droplet size, and/or preferably as suspension (dispersion) that contains the relevant chemical elements, in general, in the form of fine precipitation, e.g., in the form of a chemical mixed precipitation. The use of brines and gels has also been especially proven, especially those that contain the relevant chemical elements in an essentially homogeneous distribution and preferably those that exhibit an adhesion and flow behavior that is favorable for the subsequent coating. The starting compounds for the selected chemical elements can be, in principle, the elements themselves, advantageously in finely distributed form, in addition, all of the compounds that contain the selected chemical elements in a suitable way, such as oxides, hydroxides, oxide hydroxides, inorganic salts, preferably nitrates, carbonates, acetates, and oxalates, metal-organic compounds, alkoxides, etc. Each starting compound can be used in solid form, in the form of solutions, emulsions, and/or in the form of suspensions.

In addition, the fluid mixture can contain additional compounds that influence the adhesive properties and the flow behavior of the fluid mixture on the face to be coated. Here, as organic compounds, e.g., ethylene glycol or glycerin, like those described in DE-A 44 42 346, or, e.g., maleic acid co-polymers and as inorganic compounds, e.g., SiO₂, Si-organic compounds, or siloxanes are to be named. /8

Furthermore, the mixtures used can also contain an inorganic and/or organic binder or a binder system that stabilizes the mixture being used. For this purpose, e.g., binders or binder systems that contain metal salts, metal oxides, metal oxide hydroxides, metal-oxide hydroxide phosphates, and/or eutectic compounds melting at the temperature of use of the catalyst.

The mixture can be further set through the addition of acids and/or bases in a defined pH range. In many cases, pH-neutral suspensions are used. The mixture can be set advantageously to a pH value between 5 and 9, advantageously between 6 and 8. Special results are to be achieved with the method according to the invention when the mixture has a high solids percentage of up to 95 wt%, advantageously 50-80 wt% for a low viscosity.

In one preferred embodiment of the invention, the mixture is stirred after and, in general, also during the production and its flowability is measured continuously, but at least at the end of the production. This can be performed, e.g., by the measurement of the current consumption of the stirring unit. With the help of this measurement, the viscosity of the suspension can be set, e.g., by the addition of additional solvent or thickening agents, so that an optimum adhesion, layer thickness, and layer thickness uniformity on the surface to be coated results.

In another processing step, the coating is performed with the produced mixtures, preferably by means of a spraying method or by dipping, onto various parts of a metallic reactor tube or the tubes of a tube-bundle reactor, in particular, onto the tube inner walls, in layer having a thickness of 10-1000 µm, advantageously 20-500 µm, especially preferably 50-350 µm. /9

Furthermore, the mixture can be cast in the individual tubes and centrifuged at rotational speeds between 200 and 1000 rpm, advantageously at rotational speeds between 300 and 800 rpm. In one preferred embodiment, the coatings on the inside of the reactor tubes are produced by the spraying of the fluid mixture named above. The sprayed mixture material here presses into the uneven areas of the underlying surface, thereby preventing air bubbles under the coating. Here, the mixture that is used can adhere completely onto the sprayed inside. However, a part of the mixture can also be discharged again through dripping, particularly, for the case of small adhesion and/or low viscosity of the mixture. The auxiliary carriers to be coated, e.g., in the form of inner tubes, can be coated completely or only partially. Here, in particular, respective input reactor tubes and output reactor tubes can be omitted from the coating by a suitable device, in order to prevent sealing problems from occurring at a later time with the feed and discharge devices to be connected for the fluid. A coating has also been established whereby the mixture is sprayed into the preheated tube or this mixture is introduced by means of dipping into the preheated tube. For this purpose, the metallic base body is preheated before the spraying of the suspension to 60-500°C, preferably 200-400°C, and especially preferably 200-300°C and coated with the mixture described above at this temperature. Here, a large part of the volatile components of the mixture is evaporated and an advantageously 10-2000 µm, preferably 20-500 µm, especially preferably 50-350 µm thick layer of the catalytically active metal oxides is formed on the metallic base body. This type of production can be performed as described in DE-A-25 10 994 with the variant wherein the mixture is not deposited on a preheated carrier, but instead on a preheated, metallic base body.

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Deleted: variant wherein the

For achieving especially thick layers or especially homogeneous coatings, the coating of the reactor tubes can also be performed several times one after the other. Here, separate drying and/or calcining and/or sintering steps can be interposed between the individual coating processes of one reactor tube. The inner wall coating is advantageously performed in the case of the spraying with the help of one or

more spraying lances, advantageously with one or more moving spraying lances. Here, the spraying lance is pulled during the spraying process, e.g., with the help of an automatic device at a defined constant or varying speed, through the tube to be coated.

The thickness of the deposited layer after drying and optional calcining or sintering equals advantageously 10-1000 μm , especially preferably 20-500 μm .

In addition, the adhesion of the catalytic layer can be increased by a chemical, physical, or mechanical pretreatment of the inner tube before the coating. For the chemical pretreatment, the inner tubes can be, e.g., etched with bases or preferably with acids. Furthermore, e.g., the inner tube could be roughened by jets with a dry jet medium, in particular, corundum or quartz sand, in order to support the adhesion. In addition, cleaning agents have also been proven that represent a suspension of hard particles, e.g., corundum, in a dispersion fluid.

By heating the coated tube-bundle reactor under a vacuum or under a defined gas atmosphere to temperatures of 20-1500°C, preferably 60-1000°C, especially preferably 200-600°C, very especially preferably 250-500°C, the previously deposited coating is freed by the drying of preferably aqueous solvent. For an elevated temperature, sintering or calcining of the particles forming the coating can also take place. In this process, as a rule the actual catalytically active coating is obtained. /11

In one construction of the invention with respect to a method for the production of (meth)acrolein and (meth)acrylic acid due to catalytic gas-phase oxidation of $\text{C}_1\text{-C}_6$ alkanes, $\text{C}_2\text{-C}_6$ alkenes, $\text{C}_1\text{-C}_6$ alkanols, and/or alkanals and/or precursors under the use of a metallic reactor tube described above with catalytic coating or a tube-bundle reactor described above with reactor tubes with catalytic coating. In this method, because the risk of the formation of the risk of hot spots is avoided, processing can be done at an elevated temperature, in particular, a temperature higher by approximately 20-100°C than for the

conventional catalytic gas-phase oxidation, typically in the range of approximately 200-250°C. Due to the increased temperature, an improved educt desorption with less total combustion takes place.

The invention will be explained in detail below with reference to embodiments.

To a reactor tube with an inner diameter of 21 mm and a length of 90 cm, a mixing gas was added of 300 NI/h of the composition:

3 vol% propene,
9.5 vol% oxygen, and
the remainder nitrogen.

A multi-metal oxide catalyst of the net composition $\text{Mo}_{12}\text{W}_2\text{Bi}_1\text{Co}_{5.5}\text{Fe}_3\text{Si}_{1.6}\text{K}_{0.08}\text{O}_x$ was introduced /12 into the reactor tube in the specified form. The reaction temperatures as well as the selectivity of the reaction to acrolein and acrylic acid or to CO_2 are to be taken from the following table.

Example 1 (comparison):

The catalyst was filled into the reactor tube as a uniform catalyst in a ring shape with the measurements:

outer diameter x height x inner diameter = 5 x 3 x 2 mm.

With this conventional reaction control, the percentage of total combustion expressed by the selectivity of the reaction of CO_x (4.8% or 6.5%) is relatively high.

Example 2:

A calcined catalyst of the net composition specified above was ground, then 100 g of this powder was mixed intimately with 100 g glycerin and the resulting suspension was deposited through dipping onto the inside of a reactor tube with the dimensions specified above at room temperature. The tube was

then heated at 300°C for 2 h. The coating process was then repeated and a multi-metal oxide catalyst layer (35 g active mass) was obtained after coating twice.

Due to the use of the catalyst according to the invention as a coating of the inner wall of the reactor tube, the selectivity of the reaction with respect to acrolein and acrylic acid is improved significantly. Even at an elevated reaction temperature (400°C) relative to comparison Example 1, a higher selectivity to acrolein and acrylic acid (95.6%) relative to a selectivity of only 93.2% at a lower reaction temperature of 360°C is achieved.

Example 3:

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In a tube coated according to Example 2, a stainless steel spiral with a wall width of 1.5 cm and a wall thickness of 2 mm for intense gas turbulence was installed and tested.

The gas mixture improved by the installation of the stainless-steel spiral leads to improved selectivity of the reaction to acrolein and acrylic acid.

Example 4:

The spiral from Example 3 was coated analogous to the coating in Example 2 with a catalyst powder/glycerin mixture through dipping (10 g active mass on the spiral coil) and tested.

Through coating of the stainless steel spiral with the multi-metal oxide catalyst, the selectivity is improved significantly.

Example 5:

In a tube that was coated analogous to Example 2 (35 g active mass on the tube inside) 100 g of conventional uniform catalyst according to Example 1 was installed in the reactor outlet. The bulk height equaled 30 cm.

Through the combined use of the catalyst as a coating and simultaneously as a uniform catalyst, a significant improvement of the selectivity relative to the conventional use of the catalyst, as a uniform catalyst, was achieved.

The selectivity improvement achieved with the reactor tubes coated according to the invention leads to a clear improvement of the economy of the industrial processing.

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Example	Catalyst	Reaction temperature [°C]	Selectivity to acrolein and acrylic acid [%]	Selectivity to CO _x [%]
1	310 g catalyst rings (5*3*2) conventional	325	95.0	4.8
1	310 g catalyst rings (5*3*2) conventional	360	93.2	6.5
2	35 g catalyst coated inside tube	360	97.4	2.4
2	35 g catalyst coated on inner	400	95.6	4.2

	tube side			
3	35 g catalyst coated on inner tube side	360	97.1	2.2
3	35 g catalyst coated on inner tube side	400	96.0	3.5
4	35 g catalyst coated on inner tube side and spiral coil (10 g catalyst coated)	360	97.8	2.0

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Example	Catalyst	Reaction temperature [°C]	Selectivity to acrolein and acrylic acid [%]	Selectivity to CO _x [%]
4	35 g catalyst coated on inner tube side and spiral coil (10 g catalyst coated)	400	97.9	1.5

1. Metallic reactor tube with catalytic coating characterized in that the coating contains a multi-metal oxide mass with molybdenum and bismuth that is deposited directly on the reactor tube.

2. Reactor tube according to Claim 1, characterized in that the multi-metal oxide mass contains molybdenum, calculated as MoO_3 , in a percentage of 20-90 wt%, preferably 30-80 wt%, especially preferably 40-70 wt%.

3. Reactor tube according to Claim 1 or 2, characterized in that the catalytic coating is deposited on the tube inner wall.

4. Reactor tube according to one of Claims 1-3, characterized in that the catalytic coating has a layer thickness of 10-1000 μm , advantageously 20-500 μm , especially preferably 50-350 μm .

5. Tube-bundle reactor with reactor tubes according to one of Claims 1-4.

6. Tube-bundle reactor according to Claim 5, characterized in that a bulk material made from multi-metal oxide uniform catalysts or coated catalysts is introduced into the reactor tubes, in particular, with a filling height of 5-90%, advantageously 10-70%, especially 20-50% of the reactor tube length.

7. Tube-bundle reactor according to Claim 5 or 6 with a second reactor, in particular, a tube-bundle reactor, connected downstream with a bulk material made from multi-metal oxide uniform catalysts or coated catalysts.

8. Method for the production of coated reactor tubes according to one of Claims 1-4 or of tube-bundle reactors according to one of Claims 5-7 that comprises the following steps:

(1) Production of solutions, emulsions, and/or dispersions of elements and/or element compounds of the elements present in the multi-metal oxide catalyst and/or catalyst precursor,

(2) Optional application of adhesives, bonding agents, viscosity regulators, and/or pH-regulating means in the solutions, emulsions, and/or dispersions,

(3) Application of the solutions, emulsions, and/or dispersions on the reactor tube or the reactor tubes of the tube-bundle reactor, preferably its inside, advantageously through spraying or dipping, and

(4) Heating of the coated reactor tube, optionally in the presence of inert or reactive gases, to a temperature in the range of 20-1500°C, preferably to 200-400°C, for drying and optionally sintering or calcining the multi-metal oxide catalysts and/or catalyst precursors.

9. Method for the production of (meth)acrolein and/or (meth)acrylic acid through catalytic gas phase oxidation of C₁-C₆ alkanes, C₂-C₆ alkenes, C₁-C₆ alkanols, and/or alkanals, and/or precursors to these materials under the use of a reactor tube according to one of Claims 1-4 or a tube-bundle reactor according to one of Claims 5-7.

INTERNATIONAL SEARCH REPORT

International Patent Classification (IPC) or to both national classification and IPC According to International Patent Classification (IPC) or to both national classification and IPC		
A. CLASSIFICATION OF SUBJECT MATTER IPC 6 B01J23/31 B01J37/02 B01J19/24 B01J8/06 C07C51/25 C07C57/04 C07C45/35 C07C47/22		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 B01J C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No.	
Y	WO 92 13637 A (VEG GASINSTITUUT NV ;IND (NL)) 20 August 1992 see page 3, line 4 - line 19 see page 4, line 16 - line 21 see page 7, line 1 - line 8 see page 7, line 21 - line 29	1,2,8,9
Y	US 3 679 603 A (ISCHERIKOVA GALINA ANTONOVA ET AL) 25 July 1972 see abstract see column 2, line 56 - line 58; examples 1-3	1,2,8,9
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INTERNATIONAL SEARCH REPORT

International Application No.
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C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevance to claim No.
A	DE 21 18 871 A (BADISCHE ANILIN- & SODA-FABRIK AG) 26 October 1972 cited in the application see page 1, line 11 - line 22 see page 2, line 20 - line 29 see page 3, line 20 - line 36 -----	1-8
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